



# PATENT SPECIFICATION

NO DRAWINGS

954209

Date of Application and filing Complete Specification: July 19, 1960.  
No. 25160/60.

Application made in United States of America (No. 828,051) on July 20, 1959.

Application made in United States of America (No. 19990) on April 5, 1960.

Complete Specification Published: April 2, 1964.

© Crown Copyright 1964.

Index at acceptance:—B1 X46; C1 A13

International Classification:—B 01 d (C 01 b)

## COMPLETE SPECIFICATION

### Improvements in or relating to a Defoaming Composition and method

We, HERCULES POWDER COMPANY, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 900 Market Street, City of Wilmington, Zone 99, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in defoaming compositions and processes which are particularly useful for preventing or abating foam in aqueous systems. The invention also includes a method of preparing the compositions.

Commercial silicone defoamers have proved very effective for preventing and/or abating foam in aqueous systems. Such defoamers, however, are relatively costly and hence add appreciably to the cost of the process and/or product in which they are used.

According to the present invention, there is provided a defoaming composition comprising from 80 to 97 parts of a water-insoluble, hydrophobic, nonpolar, organic liquid having suspended therein from 20 to 3 parts of silica which has been treated to render the surface thereof hydrophobic, said surface being inert to the action of the other ingredients of the composition, and up to 5% of a spreading agent for the organic liquid based on the total weight of organic liquid, silica and spreading agent. Relatively small amounts of this composition have been found to be highly effective in suppressing or controlling foam formation in aqueous systems. The compositions may be utilized as such or in the form of aqueous emulsions.

By "spreading agent" is meant a substance having surface activity which will act to spread the hydrophobic silica and organic liquid over the surface of a liquid to be defoamed.

Having described the invention generally,

the following examples are given to illustrate specific embodiments thereof.

#### EXAMPLE 1

A defoamer was prepared as follows. A colloidal, precipitated silica was sprayed with 15% by weight, based on the weight of silica, of a dimethylpolysiloxane oil, having a viscosity of 50 centistokes. The resulting mixture was heated to 275°C. for one hour. After cooling, 10 parts of the treated silica were added to 85 parts of a naphthenic mineral oil having a Saybolt viscosity of about 80 seconds. The resulting mixture was passed through a Mantin-Gaulin homogenizer at 3000 p.s.i. pressure. To the resulting material 3 parts of commercial stearic acid and 2 parts of triethanolamine were added, and the mixture warmed to 60°C. to dissolve the stearic acid.

#### EXAMPLE 2

The procedure of Example 1 was followed except that the silica was treated by exposing it to the vapours of dichlorodimethyl silane for one hour, with agitation, instead of using the dimethylpolysiloxane oil.

#### EXAMPLE 3

The procedure of Example 1 was followed except that the silica used was obtained by displacing the water from a silica hydrogel by adding a low-boiling, water-miscible organic liquid, heating in an autoclave above the critical temperature of the liquid and then venting the autoclave.

#### EXAMPLE 4

The procedure of Example 1 was followed, except that the silica was obtained by recovering the smoke produced by the burning of silicon tetrachloride.

#### EXAMPLE 5

The procedure of Example 1 was followed except that a paraffinic oil (commonly known as a "white oil") having a Saybolt viscosity of 85 seconds was used in place of the naphthenic oil.

Defoamer efficiencies of the defoamers of Examples 1—5 were tested as follows. One

hundred and fifty (150) ml. of fresh concentrated black liquor obtained from a pulp mill were shaken vigorously at 90°C. in a 500 ml. flask having an internal diameter of 4.5 cm.

- 5 The foam level at the end of the shaking period was 3 inches. Two hundred parts per million of defoamer was then added and the mixture again shaken for one minute. The foam level at the end of this shaking period
- 10 in all cases was from about 0 to about 0.2

inches. This may be expressed as a defoaming efficiency of 0—0.2 inches.

#### EXAMPLES 6—16

Following the procedure of Example 1, a number of defoamers were prepared utilizing various spreading agents and various oils. These were tested for defoamer efficiency in the manner described above. The data is set forth in the following table.

15

TABLE

Example No.	Spreading Agent	Oil	Silica	Defoaming Efficiency Inches
6	3% Sorbitan Trioleate	85% Naphthenic Mineral Oil	12% Silica	0.2
7	3% Sorbitan Monostearate	85% Naphthenic Mineral Oil	12% Silica	0.2
8	3% Polyoxyethylene Sorbitan Tristearate	85% Naphthenic Mineral Oil	12% Silica	1.0
9	5% Sodium Stearate	85% Naphthenic Mineral Oil	10% Silica	0—0.2
10	5% Triethanolamine Stearate	85% Naphthenic Mineral Oil	10% Silica	0—0.2
11	3% Morpholinium Ethosulfate	85% Naphthenic Mineral Oil	12% Silica	0.5
12	5% Triethanolamine Stearate	85% Naphthenic Mineral Oil	10% Silica	0—0.2
13	5% Triethanolamine Stearate	85% Paraffinic Mineral Oil	10% Silica	0—0.2
14	5% Triethanolamine Stearate	85% Chlorinated Naphthenic Mineral Oil	10% Silica	0—0.2
15	5% Triethanolamine Stearate	85% Chlorinated Paraffinic Mineral Oil	10% Silica	0—0.2
16	5% Triethanolamine Stearate	85% Liquid Trifluoro Vinyl Chloride Polymer	10% Silica	0—0.2

## EXAMPLE 17

Three emulsions were prepared utilizing the following ingredients in the indicated amounts.

	Emulsion #1	Emulsion #2	Emulsion #3
*Defoamer	36.26	36.26	36.26
Polyvinyl Alcohol	0.46		
Gelatin		0.91	
Methyl Cellulose	0.91	0.46	1.37
Sorbitan Tristearate	1.82	1.82	1.82
Water	60	60	60

\* Defoamer prepared following the procedure of Example 1.

In the preparation of these emulsions the polyvinyl alcohol and methyl cellulose (Emulsion #1), the gelatin and methyl cellulose (Emulsion #2) and the methyl cellulose (Emulsion #3) were dissolved in water. The sorbitan tristearate was dissolved in the defoamer by heating to 50°C. and was then cooled to room temperature. The oil phase was added to the water phase and stirred with a Lightning Mixer. This blend was then passed through a Mantin-Gaulin Homogenizer at 500 p.s.i. These emulsions were tested for defoaming efficiencies in the manner described above utilizing 600 p.p.m. of emulsion. In all cases defoaming efficiencies were in the range 0.2—0.5 inch.

## EXAMPLE 18

Colloidal amorphous silica prepared by precipitation from sodium silicate solution and having a particle size less than 1 micron was exposed to methyl chlorosilane vapors until reaction at the surface of the silica was complete. Fifteen parts of the thus treated silica was ball-milled into 85 parts of a naphthenic mineral oil (Gulf Oil 560) until completely dispersed. Then 3.2 parts of single-pressed stearic acid (HYFAC 410) was dissolved in the mixture at 60°C. following which 1.9 parts of triethanolamine was added and stirred into the mixture.

The composition prepared as above described was evaluated as a defoamer in comparison with a well-known commercial silicone defoamer. This evaluation was carried out as follows. Two hundred fifty milliliters of concentrated black liquor (filtrate water from the first washer of an alkaline pulping system) was heated to 90°C. Two hundred parts per million of each of the commercial silicone defoamer and the defoamer prepared as above described was added to the above liquid in

separate graduates. Each was shaken vigorously for periods of 10 seconds, 30 seconds and 1 minute. 0.5 cm. of foam developed in the liquid containing the commercial silicone defoamer, whereas no foam developed in the liquid containing the defoamer prepared in accordance with the invention.

## EXAMPLE 19

Fifteen parts of colloidal silica prepared by precipitation from sodium silicate solution and having a particle size less than 1 micron was dispersed in 85 parts of naphthenic mineral oil. To this was added 10.6 parts of a polymeric silicone fluid containing some unhydrolyzed chlorine-silicon bonds and the mixture ball-milled until thoroughly dispersed. Then 3.2 parts of stearic acid (HYFAC 410) was dissolved in the above mixture at 60°C. following which 1.9 parts of triethanolamine were added to the mixture. The composition was then evaluated as a defoamer as set forth in Example 5 and the results obtained were equivalent to the results obtained for Examples 1 to 5.

An important feature of the present invention is that these novel defoamer compositions may be prepared from a variety of relatively inexpensive, water-insoluble, hydrophobic, monopolar, organic liquids. Organic liquids of this type having low surface tension, i.e., below 35—40 dynes/cm. are preferred. Exemplary of the nonpolar organic liquids which may be used herein are mineral hydrocarbons such as naphthenic mineral oils, paraffinic mineral oils, kerosene and similar petroleum fractions including food-grade mineral oil, fluorinated hydrocarbons such as Hooker Chem. Co. "Fluorolube", a liquid trifluoro vinyl chloride polymer, as well as chlorinated organic compounds such as the chloronaphthalenes, i.e., monochloronaphthalene.

The hydrophobic silica contemplated for use herein may be prepared from any of the well-known forms of silica such as (1) silica aerogel, a colloidal silica which may be prepared by displacing the water from a silica hydrogel by a low-boiling, water-miscible, organic liquid, heating in an autoclave or the like above the critical temperature of the liquid, and then venting the autoclave, (2) so-called fume silica, a colloidal silica obtained by burning silicon tetrachloride and collecting the resulting silica smoke and (3) a precipitated silica prepared by the "destabilization of a water-soluble silica under conditions which do not permit the formation of a gel structure, but rather cause the flocculation of silica particles into coherent aggregates such as by the addition of sodium ions to a sodium silicate solution."

A variety of methods may be employed for treating the normally hydrophilic silica to render it hydrophobic. One method which has proved very satisfactory involves spraying the silica with silicone oil, i.e., dimethylpolysiloxane, and heating at elevated temperature, i.e., from 250°C. to 350°C., for  $\frac{1}{2}$  to 2 hours. The amount of silicone oil utilized may vary from 5% to 100% by weight based on the weight of the silica. However, amounts from 7% to 25% will usually be satisfactory and are preferred.

The finely divided silica may also be rendered hydrophobic by treatment with vapors of an organo-silicon halide or mixture of organo-silicon halides. Examples of organo-silicon halides suitable for this purpose are given in U.S. 2,306,222 and U.S. 2,412,470 and include alkyl (methyl), aryl (phenyl), alkaryl (toyl) and aralkyl (phenyl methyl) silicon halides. The treatment may be carried out by agitating the finely divided material in a closed container in the presence of vapours of the treating material, i.e., dimethyl dichlorosilane. The amount of treating material and the length of treatment will depend upon the surface area of the inorganic material and the nature of the organo-silicon halide employed. In general, it will be satisfactory to use from 5% to 15% by weight of treating agent based on the weight of silica and a time of treatment from  $\frac{1}{2}$  to 2 hours.

Still another method of rendering the silica hydrophobic is by dispersing it in silicone oil, i.e., in a concentration from 2—10% and heating the dispersion to 250—300°C. for about an hour more or less. The hydrophobic silica may then be extracted by centrifuging the mixture after dilution with hexane or a similar type of solvent and drying the resulting solid.

Other methods of rendering the silica hydrophobic include treating the silica with an alcohol, eg. butanol, under high temperature and pressure, and coating silica with a polymer, for example, by coating the silica particles with a polymerization initiator, and contacting the

coated particles with the gaseous monomer to produce a coating of the polymer on the silica particles.

The hydrophobic silica utilized in the novel compositions of the invention will desirably have an average particle size less than 10 microns and preferably less than 5 microns. Most preferred is an average particle size from 0.02 micron to 1 micron.

The spreading agent is necessary in the defoaming compositions of the invention to allow the water-insoluble, nonpolar, organic liquid to spread adequately at the air-liquid interface to cover the whole of the surface of the liquid being defoamed. Anionic, cationic or non-ionic spreading agents, which will function in this way, are suitable for use herein. The particular type of spreading agent to be utilized is determined to some extent by the type of system in which it is used. In general, the anionics appear to give the best defoaming efficiencies and are preferred. Examples of suitable anionic spreading agents are fatty acids containing from 12 to 22 carbon atoms such as stearic and soaps of these fatty acids such as the alkali metal, alkali earth metal, aluminum, ammonium and amine soaps, i.e., triethanolamine stearate, as well as rosin soaps. The soaps may be added as such or formed in situ. Examples of other suitable anionic spreading agents are alkali metal salts of alkyl-aryl sulfonic acids, sodium dialkyl sulfo-succinate, sulfated or sulfonated oils, e.g., sulfated castor oil, sulfonated tallow, and alkali metal salts of short chain petroleum sulfonic acids.

Examples of suitable cationic spreading agents are salts of long chain (i.e., from 8 to 35 carbon atoms) primary, secondary, or tertiary amines, such as oleylamine acetate, cetylamine acetate, di-dodecylamine lactate, the acetate of aminoethyl-aminoethyl stearamide, dilauroyl triethylene tetramine diacetate, 1-aminoethyl-2-heptadecenyl imidazoline acetate; and quaternary salts, such as morpholinium ethyl sulfate, cetylpyridinium bromide, hexadecyl ethyl morpholinium chloride, and diethyl didodecyl ammonium chloride.

Examples of suitable nonionic spreading agents are condensation products of higher fatty alcohols i.e., alcohols containing from 8 to 35 carbon atoms) with ethylene oxide, such as the reaction product of oleyl alcohol with 10 ethylene oxide units; condensation products of alkylphenols with ethylene oxide, such as the reaction product of isooctylphenol with 12 ethylene oxide units; condensation products of higher fatty acid amides with 5, or more, ethylene oxide units; polyethylene glycol esters of long chain fatty acids, such as tetraethylene glycol monopalmitate, hexaethyleneglycol monolaurate, nonaethyleneglycol monostearate, nonaethyleneglycol diolate, tridecaethyleneglycol monoarachidate, tricosaeethylene glycol monobehenate, tricosaeethyleneglycol dibehen-

ate, ethylene oxide condensation products of polyhydric alcohol partial higher fatty acid esters, and their inner anhydrides (mannitol-anhydride, called Mannitan, and sorbitol-anhydride, called Sorbitan), such as glycerol monopalmitate reacted with 10 molecules of ethylene oxide, pentaerythritol monooleate reacted with 12 molecules of ethylene oxide, sorbitan monostearate reacted with 10 to 15 molecules of ethylene oxide, mannitan monopalmitate reacted with 10 to 15 molecules of ethylene oxide; long chain polyglycols in which one hydroxyl group is esterified with a higher fatty acid and the other hydroxyl group is etherified with a low molecular alcohol, such as methoxypolyethylene glycol 550 monostearate (550 meaning the average molecular weight of the polyglycol ether). A combination of two or more of these spreading agents may be used; e.g., a cationic may be blended with a nonionic; or an anionic with a nonionic.

The proportions of ingredients in the compositions of the invention may be varied widely. In general, defoaming efficiencies appear to increase with increasing proportions of solids. However, when the proportion of solids is too high, handling difficulties are encountered. Therefore, in order to retain fluidity of the product to allow ease in handling during use, the proportion of solids should not exceed 20% and preferably 15% by weight of the composition. It is possible to use as little as 3% of solids although it is preferred to use at least 10%.

The proportion of water-insoluble hydrophobic nonpolar organic liquid may vary from 97% to 80% of the composition. The preferred range is from 85% to 90%.

The amount of spreading agent used will depend on the particular composition and the particular spreading agent. In some cases as little as 0.5% by weight based on the weight of the composition, or even less, may be used. Generally, however, it will be desirable to use at least 2% of this material and not more than 5% will be required. The preferred range is from 1% to 3%.

In preparing the compositions of the invention, finely divided silica is first treated to render it suitably hydrophobic. The treated silica is then dispersed in the water-insoluble, hydrophobic, nonpolar, organic liquid. The spreading agent may be added at any convenient time prior to, during, or after dispersion of the hydrophobic silica in the liquid. The hydrophobic silica may be dispersed in the liquid by means of usual dispersing equipment such as colloid mills, or homogenizers. A ball mill may also be used. If desired, the particle size of the silica may be reduced to the desired range prior to treatment to render it hydrophobic. This may be accomplished quite effectively by an air mill. Following this the silica may then be treated to render it hydrophobic

and dispersed in the liquid in any suitable manner as by a homogenizer.

The compositions of the invention may be utilized as such by merely adding a small amount, i.e., from 0.003% to 1% and preferably from 0.003% to 0.5% to the aqueous system in which control of foaming is desired. Alternatively, these compositions may be converted to aqueous emulsions by adding water and usually an emulsifying agent and then vigorously agitating, usually by passage through a colloid mill, or homogenizer, the amount of the emulsifying agent added depending on the amount of water employed in the emulsion. Any suitable emulsifying agent such as a mixture of an equal weight per cent of sorbitan monostearate and polyoxyethylene sorbitan monostearate, the emulsifier mixtures employed in Example 17 and so on, may be utilized for the purpose and it is conceivable that the emulsifying agent may be the same as the spreading agent already present. From 3% to 10% of the emulsifier based on the oil phase will usually suffice. The amount of water utilized in the preparation of these emulsions may vary from 40% upward to 97 to 99%, depending on the desired solids content of the emulsion.

The defoamer compositions of the present invention are highly advantageous because of their low cost and high efficiencies which are equivalent to, and in some cases, surpass those of very expensive prior art defoamers costing many times as much. Moreover, the defoamer compositions of the invention retain their efficiencies in a given system much longer than most other commercial defoamers.

#### WHAT WE CLAIM IS:—

1. A defoaming composition comprising from 80 to 97 parts of a water-insoluble, hydrophobic, nonpolar, organic liquid having suspended therein from 20 to 3 parts of silica which has been treated to render the surface thereof hydrophobic, said surface being inert to the action of the other ingredients of the composition, and up to 5% of a spreading agent for the organic liquid, based on the total weight of organic liquid, silica and spreading agent.

2. A defoaming composition as claimed in Claim 1, in which the composition is in the form of an aqueous emulsion.

3. A defoaming composition as claimed in Claim 1 or 2, comprising from 85 to 90 parts of the organic liquid, from 15 to 10 parts of the hydrophobic silica and from 1 to 3%, based on the total composition, of the spreading agent.

4. A defoaming composition as claimed in any preceding claim, in which the water-soluble, hydrophobic, nonpolar organic liquid is a petroleum hydrocarbon or a fluorinated hydrocarbon.

5. A defoaming composition as claimed in

Claim 4 in which the petroleum hydrocarbon is a naphthenic oil, a paraffinic oil or kerosene.

6. A defoaming composition as claimed in Claim 4, in which the fluorinated hydrocarbon is a liquid trifluorovinyl chloride polymer.

7. A defoaming composition as claimed in any preceding claim, in which the spreading agent is an anionic, a cationic or a non-ionic spreading agent.

8. A defoaming composition as claimed in Claim 7, in which the anionic spreading agent is a fatty acid containing from 12 to 22 carbon atoms, a soap of such a fatty acid, or an alkali metal salt of an alkyl-aryl sulphonic acid.

9. A defoaming composition as claimed in Claim 7, in which the cationic spreading agent is a salt of a long chain (i.e., from 8 to 35 carbon atoms) primary, secondary or tertiary amine or a quaternary ammonium salt.

10. A defoaming composition as claimed in Claim 7, in which the non-ionic spreading agent is a condensation product of a higher

fatty alcohol (i.e., containing from 8 to 35 carbon atoms) with ethylene oxide.

11. A defoaming composition, substantially as described in any one of the foregoing Examples.

12. A process for the preparation of a defoaming composition claimed in any preceding claim, which process comprises dispersing the hydrophobic colloidal silica in the water-insoluble, hydrophobic, nonpolar, organic liquid containing the spreading agent.

13. A process for the preparation of a defoaming composition substantially as described in any one of the foregoing Examples.

14. A method of controlling foaming in an aqueous system, in which an antifoaming composition claimed in any one of Claims 1 to 11 is added to the aqueous system.

HASELTINE, LAKE & CO.,

28, Southampton Buildings,

London, W.C.2.

Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.